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## CLAIMS

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[Claim(s)]

[Claim 1] The cell component making process which a cell component is held in the sheathing material which consists of a laminate film, faces manufacturing the gel electrolyte cell which heat joining comes to enclose, carries out the laminating of a positive electrode and the negative electrode through a gel electrolyte, and is used as the above-mentioned cell component, The hold process which holds the above-mentioned cell component produced with the above-mentioned cell component making process in the above-mentioned laminate film, As opposed to the above-mentioned cell component held in the above-mentioned laminate film at the above-mentioned hold process The first heating down stream processing which heat-treats in the condition of having pressurized and is used as a cell object, The charge process which charges the above-mentioned cell object with which pressurization and heat-treatment were performed by heating down stream processing of the above first on predetermined charge conditions, The manufacture approach of the gel electrolyte cell characterized by to have the second heating down stream

processing which heat-treats where the above-mentioned cell object charged at the above-mentioned charge process is pressurized to the above-mentioned cell object which discharged at the discharge process which discharges on predetermined discharge conditions, and the above-mentioned discharge process, and is used as a cell object.

[Claim 2] The manufacture approach of the gel electrolyte cell according to claim 1 characterized by making into the range of 490kPa-2450kPa the pressure applied to the above-mentioned cell component and the above-mentioned cell object in heating down stream processing of the above first, and the second heating down stream processing.

[Claim 3] The manufacture approach of the gel electrolyte cell according to claim 1 characterized by making heat-treatment temperature over the above-mentioned cell component and the above-mentioned cell object into the range of 50 degrees C - 105 degrees C in heating down stream processing of the above first, and the second heating down stream processing.

[Claim 4] The manufacture approach of the gel electrolyte cell according to claim 1 characterized by putting the above-mentioned laminate film and the above-mentioned cell object with which the above-mentioned cell component

was held by the resin of a pair which consists of heat-resistant rubber in heating down stream processing of the above first, and the second heating down stream processing, and performing pressurization and heat-treatment.

[Claim 5] The manufacture approach of the gel electrolyte cell according to claim 1 characterized by making into 1 or less % of the weight the rate of a solvent of as [ whose boiling point under ordinary pressure it is the non-aqueous solvent contained in the above-mentioned gel electrolyte in the above-mentioned cell component making process, and is 110 degrees C or less ], to the whole non-aqueous solvent.

[Claim 6] The manufacture approach of the gel electrolyte cell according to claim 1 characterized by allotting a separator between the above-mentioned positive electrode and the above-mentioned negative electrode in the above-mentioned cell component making process.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the gel electrolyte cell equipped with the gel electrolyte.

[0002]

[Description of the Prior Art] The importance of a cell has been increasing as a power source of pocket mold electronic equipment, such as a cellular phone, and a video camera, a note type personal computer. In order to attain small lightweight-ization of electronic equipment, the light space-saving cell is called for as well as having large capacity. From such a viewpoint, the lithium cell with large energy density and output density is suitable as a power source of pocket mold electronic equipment. A discharge average electrical potential difference is more than 3.7V, and since cycle degradation at the time of the charge and discharge is also comparatively small, the lithium cell which used the carbon material for the negative electrode has the advantage which is easy to realize a high energy consistency.

[0003] the inside of a lithium cell -- flexibility -- having -- a cell with the high degree of freedom of a configuration or the sheet mold cell of a thin large area, and a thin shape -- a facet -- although cells of various configurations, such as a card mold cell of a product, are desired, it is difficult to make the cell of various

configurations which were mentioned above from the conventional technique of confining the cell component which consists of a positive electrode and a negative electrode, and the electrolytic solution in the interior of a metal sheathing can. Moreover, by using the electrolytic solution, a process becomes complicated or the need for the cure against a liquid spill comes out.

[0004] In order to solve a problem which was mentioned above, the cell using the solid electrolyte which used a conductive organic macromolecule and the conductive inorganic ceramics, and the gel solid electrolyte (a gel electrolyte is called hereafter.) which infiltrated the electrolytic solution into the matrix polymer is examined. Since the electrolyte is fixed by the solid electrolyte cell using these solid electrolytes, and the gel electrolyte cell using a gel electrolyte, a cell can be thinly made using a film-like sheathing material, and it is possible to offer energy density higher than the conventional cell.

[0005]

[Problem(s) to be Solved by the Invention] However, in a gel electrolyte cell, since the electrolytic solution is held in the matrix polymer, there is a problem that penetration of the electrolytic solution to an electrode active material layer is not fully performed. For this reason, a lithium ion cannot fully move among two

poles, but the problem that the cell capacity for which it asks as a result is unrealizable has arisen.

[0006] Furthermore, in a gel electrolyte cell, the solvent in a gel electrolyte will decompose in the case of activating charge, and gas will occur at it. When this gas occurred, the local clearance was made between the electrode active material layer and the gel electrolyte, and there was a problem that the adhesion between an electrode active material layer and a gel electrolyte will be spoiled. Migration of the lithium ion between two poles is checked, and that by which the clearance was made between the electrode active material layer and the gel electrolyte cannot realize cell capacity for which it asks except that degradation of the cell voltage under preservation serves as a defective greatly and causes the fall of the manufacture yield.

[0007] This invention is proposed in view of the conventional actual condition which was mentioned above, and it aims at offering the manufacture approach of a nonaqueous electrolyte cell that the nonaqueous electrolyte cell which has a high cell capacity is realizable while improving the fall of a poor electrical potential difference and raising the manufacture yield by maintaining the adhesion between an electrode active material layer and a gel electrolyte.

[0008]

[Means for Solving the Problem] A cell component is held in the sheathing material which the manufacture approach of the gel electrolyte cell of this invention becomes from a laminate film. The cell component making process which faces manufacturing the gel electrolyte cell which heat joining comes to enclose, carries out the laminating of a positive electrode and the negative electrode through a gel electrolyte, and is used as the above-mentioned cell component, The hold process which holds the above-mentioned cell component produced with the above-mentioned cell component making process in the above-mentioned laminate film, As opposed to the above-mentioned cell component held in the above-mentioned laminate film at the above-mentioned hold process The first heating down stream processing which heat-treats in the condition of having pressurized and is used as a cell object, The charge process which charges the above-mentioned cell object with which pressurization and heat-treatment were performed by heating down stream processing of the above first on predetermined charge conditions, It is characterized by having the second heating down stream processing which heat-treats where the above-mentioned cell object charged at the above-mentioned charge process is

pressurized to the above-mentioned cell object which discharged at the discharge process which discharges on predetermined discharge conditions, and the above-mentioned discharge process, and is used as a cell object.

[0009] Since the second heat-treatment which heat-treats in the condition pressurized, to the above-mentioned cell object which charged and discharged, and uses as a cell object has performed, even if gas occurs in the case of the above-mentioned activating-charge process and a clearance is made between a gel electrolyte and an electrode, the adhesion between a gel electrolyte and an electrode can restore and maintain by the manufacture approach of the gel electrolyte cell concerning this invention which mentioned above.

[0010]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0011] The example of 1 configuration of the gel electrolyte cell created with the application of this invention is shown in drawing 1 thru/or drawing 3 . This gel electrolyte cell 1 is equipped with the separator 5 allotted between the gel electrolyte layer 4 formed on the band-like positive electrode 2, the band-like negative electrode 3 which countered with the positive electrode 2 and was



arranged, and a positive electrode 2 and a negative electrode 3, and the positive electrode 2 with which the gel electrolyte layer 4 was formed and the negative electrode 3 with which the gel electrolyte layer 4 was formed as shown in drawing 3.

[0012] And this gel electrolyte cell 1 is covered with the sheathing film 7 with which the cell component 6 shown in drawing 2 and drawing 3 which were wound around the longitudinal direction while the laminating of the positive electrode 2 with which the gel electrolyte layer 4 was formed, and the negative electrode 3 with which the gel electrolyte layer 4 was formed is carried out through a separator 5 consists of an insulating material, and is sealed. And the positive-electrode terminal 8 is connected to a positive electrode 2, the negative-electrode terminal 9 is connected to the negative electrode 3, respectively, and these positive-electrode terminals 8 and negative-electrode terminals 9 are put between the obturation section which is the periphery section of the sheathing film 7. Moreover, the resin film 10 is arranged on the part by which the positive-electrode terminal 8 and the negative-electrode terminal 9 touch the sheathing film 7.

[0013] Positive-active-material layer 2a in which a positive electrode 2 contains

positive active material as shown in drawing 4 is formed on both sides of positive-electrode charge collector 2b. In addition, drawing 4 shows the condition that the gel electrolyte layer 4 was formed on positive-active-material layer 2a.

[0014] As this positive-electrode charge collector 2b, metallic foils, such as aluminium foil, are used, for example. As for this metallic foil, considering as a porous metal foil is desirable. The bond strength between positive-electrode charge collector 2b and positive-active-material layer 2a can be raised by using a porous metal foil as a positive-electrode charge collector. As such a porous metal foil, the metallic foil which formed much openings by etching processing besides a punching metal or an expanded metal can be used.

[0015] The lithium multiple oxide expressed with a metallic oxide, metallic sulfide, specific polymeric materials, or the general formula of  $\text{Li}_x\text{MO}_2$  as positive active material according to the class of cell made into the purpose is mentioned. In addition, M is the transition metals more than a kind, and x is usually the value of  $0.05 \leq x \leq 1.12$  within the limits.

[0016] As transition metals M which constitute the above-mentioned lithium multiple oxide, it is desirable that it is at least one sort in cobalt (Co), nickel, (nickel), or manganese (Mn). As an example of a lithium multiple oxide,  $\text{LiCoO}_2$ ,

$\text{LiNiO}_2$ ,  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  (the value of  $x$  and  $y$  changes with charge-and-discharge conditions of a cell, and are usually  $0 < x < 1$  and  $0.7 < y < 1.0$ ), or  $\text{LiMn}_2\text{O}_4$  is mentioned.

[0017] Such a lithium multiple oxide can manufacture the carbonate of a lithium compound and a transition-metals compound, for example, lithium transition metals, a nitrate, a sulfate, an oxide, a hydroxide, a halogenide, etc. as a raw material. For example, after measuring a lithium salt raw material and a transition-metals raw material according to a desired presentation, respectively and fully mixing, a lithium multiple oxide can be manufactured among an oxygen existence ambient atmosphere by carrying out heating baking in a 600 degrees C - 1000 degrees C temperature requirement. In this case, especially the mixed approach of each component is not limited, may mix fine-particles-like salts in the dry-type condition as it is, or may dissolve fine-particles-like salts in water and may mix them in the state of a water solution.

[0018] As a binder contained in positive-active-material layer 2a, the well-known resin ingredient usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.

[0019] Moreover, negative-electrode active material layer 3a in which a negative

electrode 3 contains a negative-electrode active material as shown in drawing 5 is formed on both sides of negative-electrode charge collector 3b. In addition, drawing 5 shows the condition that the gel electrolyte layer 4 was formed on negative-electrode active material layer 3a.

[0020] As this negative-electrode charge collector 3b, metallic foils, such as copper foil and a nickel foil, are used, for example. As for this metallic foil, considering as a porous metal foil is desirable. The bond strength between negative-electrode charge collector 3b and negative-electrode active material layer 3a can be raised by using a porous metal foil as a negative-electrode charge collector. As such a porous metal foil, the metallic foil which formed much openings by etching processing besides a punching metal or an expanded metal can be used.

[0021] A dope and the ingredient which can be dedoped can be used for a negative-electrode active material for a lithium. Such a lithium can be used for a lithium metal and its alloy, or a carbon material as a dope and an ingredient which can be dedoped. Specifically, carbon black, such as a natural graphite, an artificial graphite, pyrolytic carbon, corks, and acetylene black (for example, pitch coke, needle coke, petroleum coke, etc.), glassy carbon, activated carbon, a

carbon fiber, an organic macromolecule baking object (what calcinated a cellulose, phenol resin, furan resin, etc. at suitable temperature), a carbon fiber, activated carbon, etc. are mentioned as a carbon material.

[0022] As a binder contained in negative-electrode active material layer 3a, the well-known resin ingredient usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used.

[0023] As for the gel electrolyte layer 4, a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve an electrolyte salt into a non-aqueous solvent.

[0024] an electrolyte salt is independent in LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub> and LiN (CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>Li, etc. -- or it can be mixed and used. Also in it, it is desirable to use LiPF<sub>6</sub> from viewpoints, such as ion conductivity. In addition, as for the addition of an electrolyte salt, it is desirable to prepare so that it may become the concentration of 0.10 mol/l - 2.0 mol/l to a non-aqueous solvent so that good ionic conductivity may be obtained.

[0025] If the gel electrolyte with which a polymer simple substance or this was used for the matrix polymer shows the ionic conductivity of 1 or more mS/cm at a room temperature, especially chemical structure will not be limited. As this matrix

polymer, the copolymer of the copolymer of a polyacrylonitrile or a polyacrylonitrile, polyethylene oxide, or polyethylene oxide can be used, for example. As a vinyl system copolymerization monomer, hexafluoropropylene, tetrafluoroethylene, vinyl acetate, a methyl methacrylate, methacrylic-acid butyl, a methyl acrylate, butyl acrylate, an itaconic acid, hydrogenation methyl acrylate, hydrogenation ethyl acrylate, acrylamide, a vinyl chloride, vinylidene fluoride, a vinylidene chloride, etc. can be mentioned, for example. Furthermore, acrylonitrile-butadiene rubber, acrylonitrile-butadiene-styrene resin, acrylonitrile-chlorination polyethylene propylene diene styrene resin, acrylonitrile-vinyl chloride resin, acrylonitrile-methacrylate resin, acrylonitrile-acrylate resin, etc. can be used. Moreover, a polyether denaturation siloxane or its copolymer can be used. A matrix polymer which was mentioned above may use one kind independently, and even if it mixes and uses two or more sorts, it is not cared about.

[0026] independent [ in solvents, such as ethylene carbonate, propylene carbonate, butylene carbonate, gamma-butyrolactone, 2, 4-difluoro anisole, 2, 6-difluoro anisole, and 4-BUROMOBERA toll, ] as a non-aqueous solvent -- or it can mix and use.

[0027] Furthermore, when using a multilayer film like the sheathing film 7 as a sheathing material of a cell, it is desirable to use it combining a solvent [ as / whose boiling points such as ethylene carbonate, propylene carbonate, gamma-butyrolactone, 2, 4-difluoro anisole, 2, 6-difluoro anisole, and 4-BUROMOBERA toll, are 150 degrees C or more ].

[0028] Furthermore, by the gel electrolyte cell concerning the gestalt of this operation, the content of the low-boiling point solvent in a non-aqueous solvent may be 1 or less % of the weight. A low-boiling point solvent means a solvent [ as / whose boiling point under ordinary pressure is 110 degrees C or less ] here. In case it will heat-treat to a cell component and a gel electrolyte cell will be produced so that it may mention later if there are more contents of a low-boiling point solvent than 1 % of the weight, a low-boiling point solvent component will volatilize, a sheathing film will be blown up, and a cell configuration will be made to deform.

[0029] gamma-valerolactone, diethoxy ethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, methyl acetate, methyl propionate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, etc. are specifically as such a low-boiling point solvent mentioned.

[0030] As a separator 5, the fine porosity thin film which uses polyolefine as a principal component can be used. For example, polypropylene, polyethylene, or its complex can be used. It is desirable to use still more preferably the fine porosity thin film which raised the wettability to the electrolytic solution using a surfactant, corona discharge treatment, etc. Thereby, the increment in the internal resistance of a cell can be suppressed.

[0031] Although it does not limit especially about the porosity of a separator 5, it is desirable to make the porosity into 30% - 60% of range. If the porosity of a separator 5 is smaller than 30%, the output characteristics of a cell will decline greatly. Moreover, if the porosity of a separator 5 is larger than 60%, the mechanical strength of a separator 5 will fall. Moreover, although it does not limit especially about the aperture or thickness of a hole of a separator 5, either, in order to make prevention of internal short-circuit, and the shutdown effectiveness by hole lock out discover, it is desirable to set the aperture of a hole to 1 micrometer or less.

[0032] Moreover, as thickness of a separator 5, it is desirable to be referred to as 5 micrometers - about 35 micrometers. Furthermore, when the interrelation of the mechanical strength of a separator 5 and electric resistance is taken into



consideration, as for the thickness of a separator 5, it is desirable to be referred to as 7 micrometers - about 20 micrometers.

[0033] The film of the three-tiered structure which carries out the laminating of a nylon film, aluminium foil, and the polyethylene film to this order, and is made to come to rival etc. can be used for the sheathing film 7 that what is necessary is just what has dampproofing.

[0034] Since the adhesion of a gel electrolyte and an electrode active material layer is strengthened with two steps of pressurization and heat-treatment being performed to the cell component 6, while the gel electrolyte cell 1 produced with the application of this invention lessens the rate of a defective and its manufacture yield improves, this gel electrolyte cell 1 becomes what has high capacity and was excellent in the charge-and-discharge property, so that it may mention later.

[0035] And the gel electrolyte cell 1 concerning a gestait of this operation which was mentioned above is manufactured as follows.

[0036] The powder of positive active material and the need are accepted as a positive electrode 2. First, electric conduction material, such as carbon black and graphite, A mixture is prepared. binders, such as polyvinylidene fluoride, --

homogeneity -- mixing -- further -- solvents, such as dimethyl formaldehyde and n-methyl pyrrolidone, -- adding -- a paste-like positive electrode -- By [ which serve as positive-electrode charge collector 2b in it ] applying to homogeneity and drying, for example on metallic foils, such as aluminium foil, positive-active-material layer 2a is formed, and a positive-electrode sheet is produced. the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture.

[0037] Next, the gel electrolyte layer 4 is formed on positive-active-material layer 2a of a positive-electrode sheet. In order to form the gel electrolyte layer 4, first, an electrolyte salt is dissolved in a non-aqueous solvent, and nonaqueous electrolyte is produced. And a matrix polymer is added to this nonaqueous electrolyte, it agitates well, a matrix polymer is dissolved, and a sol-like electrolytic solution is obtained.

[0038] Next, specified quantity spreading of this electrolytic solution is carried out on positive-active-material layer 2a. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on positive-active-material 2a.

[0039] Next, the positive-electrode sheet with which the gel electrolyte layer 4

was formed is cut down to band-like. And the lead wire made from aluminum is welded to the agenesis part of positive-active-material layer 2a of positive-electrode charge collector 2b, and it considers as the positive-electrode terminal 8. Thus, the band-like positive electrode 2 with which the gel electrolyte layer 4 was formed is obtained.

[0040] moreover -- as a negative electrode 3 -- the powder of a negative-electrode active material, and binders, such as polyvinylidene fluoride, -- homogeneity -- mixing -- further -- solvents, such as dimethyl formaldehyde and n-methyl pyrrolidone, -- adding -- a paste-like negative electrode -- a mixture is prepared, by [ which are set to negative-electrode charge collector 3b in it ] applying to homogeneity and drying, for example on metallic foils, such as copper foil and a nickel foil, negative-electrode active material layer 3a is formed, and a negative-electrode sheet is produced. the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture.

[0041] Next, the gel electrolyte layer 4 is formed on negative-electrode active material layer 3b of a negative-electrode sheet. In order to form the gel electrolyte layer 4, specified quantity spreading of the electrolytic solution first prepared like the above is carried out on a negative-electrode active material

layer. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on negative-electrode active material 3b.

[0042] Next, the negative-electrode sheet with which the gel electrolyte layer 4 was formed is cut down to band-like. And the lead wire made from nickel is welded to the agenesis part of negative-electrode active material layer 3a of negative-electrode charge collector 3b, and it considers as the negative-electrode terminal 9. Thus, the band-like negative electrode 3 with which the gel electrolyte layer 4 was formed is obtained.

[0043] And the side in which the gel electrolyte layer 4 was formed in the band-like positive electrode 2 and band-like negative electrode 3 produced as mentioned above is made to counter, and a separator 5 is allotted between a positive electrode 2 and a negative electrode 3, and it considers as an electrode layered product between. Furthermore, this electrode layered product is wound around a longitudinal direction, and it considers as the cell component 6.

[0044] The last pinches this cell component 6 with the sheathing film 7 which consists of an insulating material, and the resin film 10 is arranged on the part with which the positive-electrode terminal 8 and the negative-electrode terminal 9, and the sheathing film 7 lap. And the periphery edge of the sheathing film 7 is

obtured, and while putting the positive-electrode terminal 8 and the negative-electrode terminal 9 between the obturation section of the sheathing film 7 and deriving outside, the cell component 6 is sealed in the sheathing film 7.

[0045] In case the cell component 6 is packed on the sheathing film 7, by arranging the resin film 10 on a contact part with the sheathing film 7, the positive-electrode terminal 8, and the negative-electrode terminal 9, the short-circuit in the weld flash of the sheathing film 7 etc. is prevented, and an adhesive property with the sheathing film 7, the positive-electrode terminal 8, and the negative-electrode terminal 9 improves.

[0046] Although especially an ingredient will not be limited if an adhesive property is shown to the positive-electrode terminal 8 and the negative-electrode terminal 9 as an ingredient of the above-mentioned resin film 10, as for polyethylene, polypropylene, denaturation polyethylene, denaturation polypropylene, these copolymers, etc., it is desirable to use what consists of polyolefin resin. Moreover, as for the thickness of the above-mentioned resin film 10, it is desirable that it is the range of 20 micrometers - 200 micrometers by the thickness in front of thermal melting arrival. If it will be dealt with if the thickness of the resin film 10 becomes thinner than 20 micrometers, and a sex worsens

and it becomes thicker than 300 micrometers, it will become difficult to become easy to penetrate moisture and to hold the airtightness inside a cell.

[0047] And in the condition of having packed with the sheathing film 7, while pressurizing the cell component 6 from the upper and lower sides, it heat-treats to the cell component 6. The cell component 6 packed with the sheathing film 7 can be pressurized, and the nonaqueous electrolyte held at the matrix polymer in a gel electrolyte can be effectively infiltrated into an electrode active material layer by heat-treating further. By infiltrating nonaqueous electrolyte into an electrode active material layer, the adhesion of the gel electrolyte layer 4 and an electrode active material layer was strengthened, it shall have high capacity and the gel electrolyte cell 1 obtained should be excelled in the charge-and-discharge property.

[0048] Since an electrolyte can be made to permeate the porous section of a separator enough especially when the positive electrode 2 with which the gel electrolyte layer 4 was formed, and the negative electrode 3 of each other with which the gel electrolyte layer 4 was formed are piled up and it constitutes them through a separator 5, the effectiveness is large.

[0049] At this time, the temperature of heat-treatment has the desirable thing to

the cell component 6 to do to more than the sol-gel transition temperature of a gel electrolyte. The direction at the time of being in a sol condition has a fluidity higher than the time of being gel, and this is because the nonaqueous electrolyte in a gel electrolyte layer can shorten penetration and heating pressurization time amount which becomes empty to an electrode active material layer.

[0050] The temperature of heat-treatment has the desirable thing to the cell component 6 to consider as the range of 50 degrees C - 105 degrees C, and, specifically, it is still more desirable to consider as the range which is 70 degrees C - 100 degrees C. If whenever [ stoving temperature ] is too higher than 105 degrees C, a part of non-aqueous solvent in a gel electrolyte will pyrolyze, and the cell capacity for which it asks will no longer be obtained. Moreover, when whenever [ stoving temperature ] is lower than 50 degrees C, the penetration of the nonaqueous electrolyte to the inside of an electrode active material layer becomes inadequate, and also the penetration of the nonaqueous electrolyte to the inside of an electrode active material layer will take time amount, and productivity will fall.

[0051] Moreover, as for the pressure applied to the cell component 6, it is desirable to consider as the range of 490kPa-2450kPa. When a pressure is

lower than 490kPa(s), the adhesion between the gel electrolyte layer 4 and an electrode active material layer becomes inadequate, and the charge-and-discharge property for which it asks is not acquired. Moreover, when a pressure is higher than 2450kPa(s), the gel electrolyte layer 4 will be crushed and will be destroyed.

[0052] Here, the pressurization and heating to the cell component 6 packed in the sheathing film 7 are performed by putting the sheathing film 7 from the upper and lower sides with a metal heat block. At this time, it is desirable to allot the block which consists of heat-resistant rubber between the sheathing film 7 and a heat block rather than to put the sheathing film 7 with a direct heat block, and to perform pressurization and heating to the cell component 6 in the sheathing film 7 through this block. If the sheathing film 7 is put with a direct heat block and \*\* thickness and heating are performed to the cell component 6, temperature maintenance of the heat block concerned will become difficult, and will become unstable [ temperature ], and also the uniform pressurization control to the cell component 6 will become difficult. Therefore, by minding the block which consists of heat-resistant rubber, to the cell component 6, it is stabilized in homogeneity and pressurization and heating can be performed to it.



[0053] A cell object is acquired according to the above process.

[0054] Next, in order to activate the acquired cell object, a cell object is charged on predetermined charge conditions. And the charged cell object is discharged on predetermined discharge conditions. What is necessary is just to set up suitably the charge-and-discharge conditions in this case if needed [, such as a configuration of a cell, and magnitude, ].

[0055] Here, when the solvent in a gel electrolyte decomposes in the case of the above-mentioned activating charge, gas will occur. There was a problem that the cell capacity for which a lithium ion cannot fully move among two poles except that a clearance local between the electrode active material layer and gel electrolyte layers 4 in case this gas occurs is made, the adhesion between the electrode active material layer and gel electrolyte layers 4 is spoiled in this part, degradation of the cell voltage under preservation is large, there is much generating of a defective and the manufacture yield falls, but it asks as a result was unrealizable.

[0056] So, in this invention, while pressurizing the cell object with which activating charge and discharge were made from the upper and lower sides, it heat-treats to a cell object. The cell object packed with the sheathing film 7 is

pressurized, and by heat-treating further, even if a clearance is made between the gel electrolyte layer 4 and an electrode active material layer by the gas which occurred on the occasion of the above-mentioned activating charge process, a gel electrolyte and an electrode can be stuck. By maintaining the adhesion of the gel electrolyte layer 4 and an electrode active material layer, there shall be no poor electrical potential difference about the gel electrolyte cell 1 obtained, and it shall have high capacity, and should excel in the charge-and-discharge property.

[0057] As for the temperature of the heat-treatment to a cell object, at this time, it is desirable to carry out to more than the sol-gel transition temperature of a gel electrolyte. As for the temperature of the heat-treatment to a cell object, it is desirable to consider as the range of 50 degrees C - 105 degrees C, and, specifically, it is still more desirable to consider as the range which is 70 degrees C - 100 degrees C. If whenever [ stoving temperature ] is too higher than 105 degrees C, a part of non-aqueous solvent in a gel electrolyte will pyrolyze, and the cell capacity for which it asks will no longer be obtained. Moreover, when whenever [ stoving temperature ] is lower than 50 degrees C, adhesion becomes inadequate about a gel electrolyte and an electrode, and also sticking a gel electrolyte and an electrode will take time amount, and productivity will fall.

[0058] Moreover, as for the pressure applied to a cell object, it is desirable to consider as the range of 490kPa-2450kPa. When a pressure is lower than 490kPa(s), the adhesion between the gel electrolyte layer 4 and an electrode active material layer becomes inadequate, and the charge-and-discharge property for which it asks is not acquired. Moreover, when a pressure is higher than 2450kPa(s), the gel electrolyte layer 4 will be crushed and will be destroyed.

[0059] Here, the pressurization and heating to a cell object are performed by putting the sheathing film 7 from the upper and lower sides with a metal heat block. At this time, it is desirable to allot the block which consists of heat-resistant rubber between the sheathing film 7 and a heat block rather than to to put the sheathing film 7 with a direct heat block, and to perform pressurization and heating to the cell object in the sheathing film 7 through this block. If the sheathing film 7 is put with a direct heat block and \*\* thickness and heating are performed to a cell object, temperature maintenance of the heat block concerned will become difficult, and will become unstable [ temperature ], and also the uniform pressurization control to a cell object will become difficult. Therefore, by minding the block which consists of heat-resistant rubber, to a cell object, it is stabilized in homogeneity and pressurization and heating can be

performed to it.

[0060] The gel electrolyte cell 1 is completed as mentioned above.

[0061] Even if a clearance is made by the gel electrolyte cell 1 produced with the application of this invention between a gel electrolyte layer and an electrode active material layer by the gas which occurred on the occasion of the above-mentioned activating charge process, it can restore the clearance, can maintain the adhesion between a gel electrolyte layer and an electrode active material layer, and can improve the manufacture yield. And the cell produced by making it such moves the lithium between forward negative electrodes smoothly, is closed, and becomes what has high capacity and was excellent in the charge-and-discharge property. Furthermore, the gel electrolyte cell 1 produced with the application of this invention becomes the thing excellent also in the dependability in an elevated temperature.

[0062] In addition, although the case where carried out the laminating of the band-like positive electrode 2 and the band-like negative electrode 3, and wound around the longitudinal direction further and it considered as the cell component 6 was mentioned as the example and the gestalt of operation mentioned above explained it, this invention is not limited to this, and when the laminating of the

rectangle-like positive electrode 2 and the rectangle-like negative electrode 3 was carried out and being considered as the electrode layered product, or also when an electrode layered product is folded up by turns, it can be applied.

[0063] The gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above is not limited especially about the configuration, and can be made into a thin shape and the various magnitude of large-sized \*\*. Moreover, this invention is [ primary cell ] applicable also about a rechargeable battery.

[0064]

[Example] As shown below, the cell was produced and the effectiveness of this invention was checked.

[0065] <Example> First, as it was the following, the positive electrode was produced. first -- as positive active material --  $\text{LiCoO}_2$  of 5 micrometers of mean diameters -- as 91 weight sections and an electric conduction agent -- carbon black -- as 6 weight sections and a binder -- polyvinylidene fluoride -- 3 weight sections -- mixing -- a positive electrode -- it considered as the mixture. furthermore, this positive electrode -- N-methyl pyrrolidone used as a solvent was distributed and the mixture was made into the shape of a paste.

[0066] next, the obtained positive electrode -- a mixture -- desiccation processing

was performed after applying a paste to homogeneity to both sides of band-like aluminium foil with a thickness of 20 micrometers it is thin to a positive-electrode charge collector. The positive-active-material layer was formed by carrying out compression molding with a roller press machine after desiccation. Furthermore, the lead made from reticulated aluminum was welded to the positive-active-material layer agensis part of a positive-electrode charge collector, it considered as the positive-electrode terminal, and the positive electrode was produced.

[0067] Next, the negative electrode was produced as it was the following. first -- as the obtained negative-electrode active material -- the graphite of 20 micrometers of mean diameters -- as 90 weight sections and a binder -- polyvinylidene fluoride -- 10 weight sections -- mixing -- a negative electrode -- it considered as the mixture. furthermore, this negative electrode -- N-methyl pyrrolidone used as a solvent was distributed and the mixture was made into the shape of a paste.

[0068] next, the obtained negative electrode -- a mixture -- desiccation processing was performed after applying a paste to homogeneity to both sides of band-like copper foil with a thickness of 15 micrometers it is thin to a

negative-electrode charge collector. The negative-electrode active material layer was formed by carrying out compression molding with a roller press machine after desiccation. Furthermore, the reticulated copper lead was welded to the negative-electrode active material layer agensis part of a negative-electrode charge collector, it considered as the negative-electrode terminal, and the negative electrode was produced.

[0069] Next, as it was the following, the gel electrolyte layer was formed in up to a positive electrode and a negative electrode.

[0070] First, ethylene carbonate, propylene carbonate, and gamma-butyl lactone dissolved LiPF<sub>6</sub> in the mixed solvent which it comes to mix at a rate of the weight ratio 5:3:2 by the concentration of 1.2 mol/l, nonaqueous electrolyte was prepared, the copolymer of vinylidene fluoride and hexafluoropropylene was further mixed at 15% of the weight of a rate to this nonaqueous electrolyte, and the polyelectrolyte solution was prepared.

[0071] Next, the obtained electrolytic solution was applied to homogeneity with the doctor blade method, respectively to both sides of the above-mentioned positive electrode and the above-mentioned negative electrode. Then, the electrolytic solution was made to gel and the gel electrolyte layer was made to

form in both sides of a positive electrode and a negative electrode.

[0072] Next, the cell was assembled as it was the following. First, the laminating of the band-like positive electrode which was produced as mentioned above and with which the gel electrolyte layer was formed in both sides, and the band-like negative electrode with which the gel electrolyte layer was formed in both sides was carried out through the separator, it considered as the layered product, and the cell component was obtained by winding this layered product around that longitudinal direction further. Here, the porous membrane made from polyethylene was used for the separator.

[0073] Next, it obturated by pinching this cell component from the outermost layer with the dampproof sheathing film with which it comes to carry out the laminating of the nylon of 25-micrometer thickness, the aluminum of 40-micrometer thickness, and the polypropylene of 30-micrometer thickness to order, and carrying out thermal melting arrival under reduced pressure of the periphery edge of a sheathing film, and the cell component was sealed in the sheathing film. In addition, while putting the positive-electrode terminal and the negative-electrode terminal between the obturation section of a sheathing film at this time, the polyolefine film was arranged on the contact part with a sheathing



film, a positive-electrode terminal, and a negative-electrode terminal.

[0074] Next, where the closure is carried out to a sheathing film, while applying the pressure of 1470kPa(s) to the cell component, first pressurization heat-treatment at 90 degrees C was performed to the cell component, and it considered as the cell object. In addition, the first [ to a cell component ] pressurization heat-treatment put the cell component by which the closure was carried out to the sheathing film with the heat block of a pair through the block made of silicone rubber.

[0075] Next, in order to activate the acquired cell object, the cell object was charged on predetermined charge conditions, and the charged cell object was discharged on predetermined discharge conditions.

[0076] While applying the pressure of 1470kPa(s) to the last to the cell object with which activating charge and discharge were made, after performing second heat-treatment at 90 degrees C to a cell object, the cell object was charged on predetermined charge conditions.

[0077] Thus, dimension 53mmx34mm and a gel electrolyte cell with a thickness of 3mm were completed. In addition, the second [ to a cell object ] pressurization heat-treatment put the cell object with the heat block of a pair through the block

made of silicone rubber.

[0078] <Example 1 of a comparison> The gel electrolyte cell was produced like the example 1 except having not performed second [ to the cell object with which activating charge and discharge were made ] pressurization heat-treatment.

[0079] <Example 2 of a comparison> In the first pressurization heat-treatment, the pressure produced the gel electrolyte cell like the example 1 to the cell component concerned only except having heat-treated without applying by holding the above-mentioned cell component in a thermostat rather than performing pressurization heat-treatment using a heat block to a cell component.

[0080] And the property was evaluated about the sample cell of the example produced as mentioned above, the example 1 of a comparison, and the example 2 of a comparison. In addition, the gel electrolyte cell produced in these examples, the example 1 of a comparison, and the example 2 of a comparison is designed so that it may have the capacity of about 500 mAh(s).

[0081] First, the yield was evaluated about 100 sample cells of an example and the example 1 of a comparison. Evaluation of the yield measured aging of the open-circuit voltage (OCV:Open-Ccircuit Voltage) from immediately after cell completion, used as the excellent article that by which the predetermined

electrical potential difference is maintained after time amount progress, and investigated the rate of the excellent article in 100 pieces. About the sample cell of these examples and the example 1 of a comparison, the relation between elapsed time(Sun.) and OCV (V) is shown in drawing 6 .

[0082] By the cell of the example 1 of a comparison which did not perform second pressurization heat-treatment to the cell object with which activating charge and discharge were carried out, between the gel electrolyte layer and the electrode active material layer, the local clearance was generated, the adhesion of a gel electrolyte layer and an electrode active material layer could not be raised, but the fall of the electrical potential difference accompanying time amount progress was also large, and the yield was only 92% so that clearly from drawing 6 .

[0083] By the cell of the example which, on the other hand, performed second heating pressure treatment to the cell object with which activating charge and discharge were carried out, between the gel electrolyte layer and the electrode active material layer, a clearance was not seen, but the adhesion of a gel electrolyte layer and an electrode active material layer was maintained, the fall of the electrical potential difference accompanying time amount progress is also

about 50mV less than the cell of the example 1 of a comparison, it was stopped, and the value with the as high yield as 96% was acquired.

[0084] Moreover, when the charge and discharge test was performed on predetermined charge-and-discharge conditions about the sample cell of the produced example and the example 1 of a comparison and discharge capacity was measured, by the cell of an example, discharge capacity was improving about 5% on the average compared with the cell of the example 1 of a comparison, and sufficient discharge capacity was obtained.

[0085] Therefore, even if a clearance is generated between an electrode active material layer and a gel electrolyte layer by the gas which occurs in the case of activating charge, by performing pressurization and heat-treatment to a cell object after discharge, this clearance can be restored and the adhesion of an electrode active material layer and a gel electrolyte layer can be raised. Thereby, it turned out that the yield of a cell can be improved greatly. And it turned out that the cell produced by making it such moves the lithium between forward negative electrodes smoothly, and is closed, and it becomes what sag is also stopped few and has the outstanding charge-and-discharge property.

[0086] Furthermore, the heating property in a high-voltage charge condition was

evaluated about the cell of an example and the example 1 of a comparison. Evaluation of a heating property was in the condition which charged the cell of an example and the example 1 of a comparison 4.25V or 4.40V, heated the cell at 135 degrees C, 140 degrees C, 145 degrees C, 150 degrees C, and 155 degrees C, and set to O.K. the case where the function as NG and a cell was maintained in the case where the function as a cell is lost. The result is shown in Table 1.

[0087]

[Table 1]

[0088] It is at the 4.25V charge time, and it is at the 4.25V charge time, it is at the 140 degrees-C and 4.40V charge time, and a cell function is maintained [ by the cell of the example which performed second heating pressure treatment to the cell object after activation charge and discharge ] only to 135 degrees C by the cell of the example 1 of a comparison which did not perform second heating pressure treatment to the cell function being maintained to 140 degrees C also in

the time of 150 degrees C and 4.40V charge so that clearly from Table 1. Thereby, by performing second heating pressure treatment to the cell object after activation charge and discharge showed that the cell obtained could be made into what has high dependability also in an elevated temperature.

[0089] Below, about the cell of an example and the example 2 of a comparison, after performing second pressurization heat-treatment the time of activating charge, and after discharge, the cell capacity was measured.

[0090] By the cell of the example which gave first pressurization heating down stream processing to the cell component, the welding between a separator, a gel electrolyte layer, and an electrode active material layer is strong. For this reason, even if gas occurs at the time of activating charge, the adhesion of a positive electrode and a negative electrode is kept generally, and a high capacity called 495mAh is obtained.

[0091] And by performing second pressurization heat-treatment, after discharging the cell of this example, welding of inter-electrode [ which was left by the generation of gas ] is carried out, and the high capacity as 500mAh(s) and a design is obtained.

[0092] On the other hand, in the first pressurization heat-treatment, by the cell of

the example 2 of a comparison which only heat-treated to the cell component, without putting a pressure, in order that a positive electrode and a negative electrode may separate by the gas which occurs at the time of activating charge since the welding of a separator, a gel electrolyte layer, and an electrode active material layer is weak and a lithium ion may not intercalate in a negative electrode, 460mAh and sufficient capacity are not obtained.

[0093] By performing second pressurization heat-treatment, after discharging the cell of this example 2 of a comparison, welding of inter-electrode [ which was left by the generation of gas ] is carried out. Although 485mAh and capacity go up after a recharge by this since a lithium ion comes to be intercalated in a negative electrode, the cell as a design is not obtained.

[0094] In addition, the cell of the example 2 of a comparison which does not perform pressurization to a cell component first of the effectiveness of the improvement in capacity by performing second pressurization heat-treatment to a cell after activation charge and discharge is larger. By the cell of the example which performs pressurization to the introduction cell component, since inter-electrode adhesion is high from the first, the improvement in capacity is seldom accepted.

[0095] However, since the cell of the example which performs pressurization to a cell component first can, on the whole, obtain the cell which has the high capacity as a design, it can be said to a cell component or a cell object that it is required to perform two heating pressure treatment before and behind activation charge and discharge.

[0096]

[Effect of the Invention] In this invention, by performing pressurization and heat-treatment to the cell object equipped with the gel electrolyte, even if a clearance is made by the gas which occurred on the occasion of activating charge between a gel electrolyte layer and an electrode active material layer, the adhesion between a gel electrolyte layer and an electrode active material layer can be restored, and the manufacture yield can be improved.

[0097] Consequently, in this invention, the gel electrolyte cell which the adhesion of a gel electrolyte layer and an electrode active material layer realizes increase and high capacity-ization, and is excellent in a charge-and-discharge property and dependability is realizable.

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## TECHNICAL FIELD

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[Field of the Invention] This invention relates to the manufacture approach of the gel electrolyte cell equipped with the gel electrolyte.

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## PRIOR ART

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[Description of the Prior Art] The importance of a cell has been increasing as a power source of pocket mold electronic equipment, such as a cellular phone, and a video camera, a note type personal computer. In order to attain small lightweight-ization of electronic equipment, the light space-saving cell is called for as well as having large capacity. From such a viewpoint, the lithium cell with large energy density and output density is suitable as a power source of pocket mold electronic equipment. A discharge average electrical potential difference is more than 3.7V, and since cycle degradation at the time of the charge and discharge is also comparatively small, the lithium cell which used the carbon material for the negative electrode has the advantage which is easy to realize a high energy consistency.

[0003] the inside of a lithium cell -- flexibility -- having -- a cell with the high degree of freedom of a configuration or the sheet mold cell of a thin large area, and a thin shape -- a facet -- although cells of various configurations, such as a card mold cell of a product, are desired, it is difficult to make the cell of various configurations which were mentioned above from the conventional technique of confining the cell component which consists of a positive electrode and a negative electrode, and the electrolytic solution in the interior of a metal sheathing can. Moreover, by using the electrolytic solution, a process becomes complicated or the need for the cure against a liquid spill comes out.

[0004] In order to solve a problem which was mentioned above, the cell using the solid electrolyte which used a conductive organic macromolecule and the conductive inorganic ceramics, and the gel solid electrolyte (a gel electrolyte is called hereafter.) which infiltrated the electrolytic solution into the matrix polymer is examined. Since the electrolyte is fixed by the solid electrolyte cell using these solid electrolytes, and the gel electrolyte cell using a gel electrolyte, a cell can be thinly made using a film-like sheathing material, and it is possible to offer energy density higher than the conventional cell.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] In this invention, by performing pressurization and heat-treatment to the cell object equipped with the gel electrolyte, even if a clearance is made by the gas which occurred on the occasion of activating charge between a gel electrolyte layer and an electrode active material layer, the adhesion between a gel electrolyte layer and an electrode active material layer can be restored, and the manufacture yield can be improved.

[0097] Consequently, in this invention, the gel electrolyte cell which the adhesion of a gel electrolyte layer and an electrode active material layer realizes increase and high capacity-ization, and is excellent in a charge-and-discharge property and dependability is realizable.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, in a gel electrolyte cell, since the electrolytic solution is held in the matrix polymer, there is a problem

that penetration of the electrolytic solution to an electrode active material layer is not fully performed. For this reason, a lithium ion cannot fully move among two poles, but the problem that the cell capacity for which it asks as a result is unrealizable has arisen.

[0006] Furthermore, in a gel electrolyte cell, the solvent in a gel electrolyte will decompose in the case of activating charge, and gas will occur at it. When this gas occurred, the local clearance was made between the electrode active material layer and the gel electrolyte, and there was a problem that the adhesion between an electrode active material layer and a gel electrolyte will be spoiled. Migration of the lithium ion between two poles is checked, and that by which the clearance was made between the electrode active material layer and the gel electrolyte cannot realize cell capacity for which it asks except that degradation of the cell voltage under preservation serves as a defective greatly and causes the fall of the manufacture yield.

[0007] This invention is proposed in view of the conventional actual condition which was mentioned above, and it aims at offering the manufacture approach of a nonaqueous electrolyte cell that the nonaqueous electrolyte cell which has a high cell capacity is realizable while improving the fall of a poor electrical

potential difference and raising the manufacture yield by maintaining the adhesion between an electrode active material layer and a gel electrolyte.

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## MEANS

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[Means for Solving the Problem] A cell component is held in the sheathing material which the manufacture approach of the gel electrolyte cell of this invention becomes from a laminate film. The cell component making process which faces manufacturing the gel electrolyte cell which heat joining comes to enclose, carries out the laminating of a positive electrode and the negative electrode through a gel electrolyte, and is used as the above-mentioned cell component, The hold process which holds the above-mentioned cell component produced with the above-mentioned cell component making process in the above-mentioned laminate film, As opposed to the above-mentioned cell component held in the above-mentioned laminate film at the above-mentioned hold process The first heating down stream processing which heat-treats in the condition of having pressurized and is used as a cell object, The charge process which charges the above-mentioned cell object with which pressurization and

heat-treatment were performed by heating down stream processing of the above first on predetermined charge conditions, It is characterized by having the second heating down stream processing which heat-treats where the above-mentioned cell object charged at the above-mentioned charge process is pressurized to the above-mentioned cell object which discharged at the discharge process which discharges on predetermined discharge conditions, and the above-mentioned discharge process, and is used as a cell object.

[0009] Since the second heat-treatment which heat-treats in the condition pressurized, to the above-mentioned cell object which charged and discharged, and uses as a cell object has performed, even if gas occurs in the case of the above-mentioned activating-charge process and a clearance is made between a gel electrolyte and an electrode, the adhesion between a gel electrolyte and an electrode can restore and maintain by the manufacture approach of the gel electrolyte cell concerning this invention which mentioned above.

[0010]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0011] The example of 1 configuration of the gel electrolyte cell created with the

application of this invention is shown in drawing 1 thru/or drawing 3 . This gel electrolyte cell 1 is equipped with the separator 5 allotted between the gel electrolyte layer 4 formed on the band-like positive electrode 2, the band-like negative electrode 3 which countered with the positive electrode 2 and was arranged, and a positive electrode 2 and a negative electrode 3, and the positive electrode 2 with which the gel electrolyte layer 4 was formed and the negative electrode 3 with which the gel electrolyte layer 4 was formed as shown in drawing 3 .

[0012] And this gel electrolyte cell 1 is covered with the sheathing film 7 with which the cell component 6 shown in drawing 2 and drawing 3 which were wound around the longitudinal direction while the laminating of the positive electrode 2 with which the gel electrolyte layer 4 was formed, and the negative electrode 3 with which the gel electrolyte layer 4 was formed is carried out through a separator 5 consists of an insulating material, and is sealed. And the positive-electrode terminal 8 is connected to a positive electrode 2, the negative-electrode terminal 9 is connected to the negative electrode 3, respectively, and these positive-electrode terminals 8 and negative-electrode terminals 9 are put between the obturation section which is the periphery section

of the sheathing film 7. Moreover, the resin film 10 is arranged on the part by which the positive-electrode terminal 8 and the negative-electrode terminal 9 touch the sheathing film 7.

[0013] Positive-active-material layer 2a in which a positive electrode 2 contains positive active material as shown in drawing 4 is formed on both sides of positive-electrode charge collector 2b. In addition, drawing 4 shows the condition that the gel electrolyte layer 4 was formed on positive-active-material layer 2a.

[0014] As this positive-electrode charge collector 2b, metallic foils, such as aluminium foil, are used, for example. As for this metallic foil, considering as a porous metal foil is desirable. The bond strength between positive-electrode charge collector 2b and positive-active-material layer 2a can be raised by using a porous metal foil as a positive-electrode charge collector. As such a porous metal foil, the metallic foil which formed much openings by etching processing besides a punching metal or an expanded metal can be used.

[0015] The lithium multiple oxide expressed with a metallic oxide, metallic sulfide, specific polymeric materials, or the general formula of  $\text{Li}_x\text{MO}_2$  as positive active material according to the class of cell made into the purpose is mentioned. In addition, M is the transition metals more than a kind, and x is usually the value of



$0.05 \leq x \leq 1.12$  within the limits.

[0016] As transition metals M which constitute the above-mentioned lithium multiple oxide, it is desirable that it is at least one sort in cobalt (Co), nickel, (nickel), or manganese (Mn). As an example of a lithium multiple oxide,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  (the value of x and y changes with charge-and-discharge conditions of a cell, and are usually  $0 < x < 1$  and  $0.7 < y < 1.0$ ), or  $\text{LiMn}_2\text{O}_4$  is mentioned.

[0017] Such a lithium multiple oxide can manufacture the carbonate of a lithium compound and a transition-metals compound, for example, lithium transition metals, a nitrate, a sulfate, an oxide, a hydroxide, a halogenide, etc. as a raw material. For example, after measuring a lithium salt raw material and a transition-metals raw material according to a desired presentation, respectively and fully mixing, a lithium multiple oxide can be manufactured among an oxygen existence ambient atmosphere by carrying out heating baking in a 600 degrees C - 1000 degrees C temperature requirement. In this case, especially the mixed approach of each component is not limited, may mix fine-particles-like salts in the dry-type condition as it is, or may dissolve fine-particles-like salts in water and may mix them in the state of a water solution.

[0018] As a binder contained in positive-active-material layer 2a, the well-known resin ingredient usually used as a binder of the positive-active-material layer of this kind of nonaqueous electrolyte cell can be used.

[0019] Moreover, negative-electrode active material layer 3a in which a negative electrode 3 contains a negative-electrode active material as shown in drawing 5 is formed on both sides of negative-electrode charge collector 3b. In addition, drawing 5 shows the condition that the gel electrolyte layer 4 was formed on negative-electrode active material layer 3a.

[0020] As this negative-electrode charge collector 3b, metallic foils, such as copper foil and a nickel foil, are used, for example. As for this metallic foil, considering as a porous metal foil is desirable. The bond strength between negative-electrode charge collector 3b and negative-electrode active material layer 3a can be raised by using a porous metal foil as a negative-electrode charge collector. As such a porous metal foil, the metallic foil which formed much openings by etching processing besides a punching metal or an expanded metal can be used.

[0021] A dope and the ingredient which can be dedoped can be used for a negative-electrode active material for a lithium. Such a lithium can be used for a

lithium metal and its alloy, or a carbon material as a dope and an ingredient which can be dedoped. Specifically, carbon black, such as a natural graphite, an artificial graphite, pyrolytic carbon, corks, and acetylene black (for example, pitch coke, needle coke, petroleum coke, etc.), glassy carbon, activated carbon, a carbon fiber, an organic macromolecule baking object (what calcinated a cellulose, phenol resin, furan resin, etc. at suitable temperature), a carbon fiber, activated carbon, etc. are mentioned as a carbon material.

[0022] As a binder contained in negative-electrode active material layer 3a, the well-known resin ingredient usually used as a binder of the negative-electrode active material layer of this kind of nonaqueous electrolyte cell can be used.

[0023] As for the gel electrolyte layer 4, a matrix polymer comes to make into gel the nonaqueous electrolyte which comes to dissolve an electrolyte salt into a non-aqueous solvent.

[0024] an electrolyte salt is independent in  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$  and  $\text{LiN}(\text{CF}_3\text{SO}_3)_2$ ,  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$ , etc. -- or it can be mixed and used. Also in it, it is desirable to use  $\text{LiPF}_6$  from viewpoints, such as ion conductivity. In addition, as for the addition of an electrolyte salt, it is desirable to prepare so that it may become the concentration of 0.10 mol/l - 2.0 mol/l to a non-aqueous

solvent so that good ionic conductivity may be obtained.

[0025] If the gel electrolyte with which a polymer simple substance or this was used for the matrix polymer shows the ionic conductivity of 1 or more mS/cm at a room temperature, especially chemical structure will not be limited. As this matrix polymer, the copolymer of the copolymer of a polyacrylonitrile or a polyacrylonitrile, polyethylene oxide, or polyethylene oxide can be used, for example. As a vinyl system copolymerization monomer, hexafluoropropylene, tetrafluoroethylene, vinyl acetate, a methyl methacrylate, methacrylic-acid butyl, a methyl acrylate, butyl acrylate, an itaconic acid, hydrogenation methyl acrylate, hydrogenation ethyl acrylate, acrylamide, a vinyl chloride, vinylidene fluoride, a vinylidene chloride, etc. can be mentioned, for example. Furthermore, acrylonitrile-butadiene rubber, acrylonitrile-butadiene-styrene resin, acrylonitrile-chlorination polyethylene propylene diene styrene resin, acrylonitrile-vinyl chloride resin, acrylonitrile-methacrylate resin, acrylonitrile-acrylate resin, etc. can be used. Moreover, a polyether denaturation siloxane or its copolymer can be used. A matrix polymer which was mentioned above may use one kind independently, and even if it mixes and uses two or more sorts, it is not cared about.

[0026] independent [ in solvents, such as ethylene carbonate, propylene carbonate, butylene carbonate, gamma-butyl lactone, 2, 4-difluoro anisole, 2, 6-difluoro anisole, and 4-BUROMOBERA toll, ] as a non-aqueous solvent -- or it can mix and use.

[0027] Furthermore, when using a multilayer film like the sheathing film 7 as a sheathing material of a cell, it is desirable to use it combining a solvent [ as / whose boiling points such as ethylene carbonate, propylene carbonate, gamma-butyl lactone, 2, a 4-difluoro anisole, 2, a 6-difluoro anisole, and 4-BUROMOBERA toll, are 150 degrees C or more ].

[0028] Furthermore, by the gel electrolyte cell concerning the gestalt of this operation, the content of the low-boiling point solvent in a non-aqueous solvent may be 1 or less % of the weight. A low-boiling point solvent means a solvent [ as / whose boiling point under ordinary pressure is 110 degrees C or less ] here.

In case it will heat-treat to a cell component and a gel electrolyte cell will be produced so that it may mention later if there are more contents of a low-boiling point solvent than 1 % of the weight, a low-boiling point solvent component will volatilize, a sheathing film will be blown up, and a cell configuration will be made to deform.

[0029] gamma-valerolactone, diethoxy ethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, methyl acetate, methyl propionate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, etc. are specifically as such a low-boiling point solvent mentioned.

[0030] As a separator 5, the fine porosity thin film which uses polyolefine as a principal component can be used. For example, polypropylene, polyethylene, or its complex can be used. It is desirable to use still more preferably the fine porosity thin film which raised the wettability to the electrolytic solution using a surfactant, corona discharge treatment, etc. Thereby, the increment in the internal resistance of a cell can be suppressed.

[0031] Although it does not limit especially about the porosity of a separator 5, it is desirable to make the porosity into 30% - 60% of range. If the porosity of a separator 5 is smaller than 30%, the output characteristics of a cell will decline greatly. Moreover, if the porosity of a separator 5 is larger than 60%, the mechanical strength of a separator 5 will fall. Moreover, although it does not limit especially about the aperture or thickness of a hole of a separator 5, either, in order to make prevention of internal short-circuit, and the shutdown effectiveness by hole lock out discover, it is desirable to set the aperture of a

hole to 1 micrometer or less.

[0032] Moreover, as thickness of a separator 5, it is desirable to be referred to as 5 micrometers - about 35 micrometers. Furthermore, when the interrelation of the mechanical strength of a separator 5 and electric resistance is taken into consideration, as for the thickness of a separator 5, it is desirable to be referred to as 7 micrometers - about 20 micrometers.

[0033] The film of the three-tiered structure which carries out the laminating of a nylon film, aluminium foil, and the polyethylene film to this order, and is made to come to rival etc. can be used for the sheathing film 7 that what is necessary is just what has dampproofing.

[0034] Since the adhesion of a gel electrolyte and an electrode active material layer is strengthened with two steps of pressurization and heat-treatment being performed to the cell component 6, while the gel electrolyte cell 1 produced with the application of this invention lessens the rate of a defective and its manufacture yield improves, this gel electrolyte cell 1 becomes what has high capacity and was excellent in the charge-and-discharge property, so that it may mention later.

[0035] And the gel electrolyte cell 1 concerning a gestalt of this operation which

was mentioned above is manufactured as follows.

[0036] The powder of positive active material and the need are accepted as a positive electrode 2. First, electric conduction material, such as carbon black and graphite, A mixture is prepared. binders, such as polyvinylidene fluoride, -- homogeneity -- mixing -- further -- solvents, such as dimethyl formaldehyde and n-methyl pyrrolidone, -- adding -- a paste-like positive electrode -- By [ which serve as positive-electrode charge collector 2b in it ] applying to homogeneity and drying, for example on metallic foils, such as aluminium foil, positive-active-material layer 2a is formed, and a positive-electrode sheet is produced. the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture.

[0037] Next, the gel electrolyte layer 4 is formed on positive-active-material layer 2a of a positive-electrode sheet. In order to form the gel electrolyte layer 4, first, an electrolyte salt is dissolved in a non-aqueous solvent, and nonaqueous electrolyte is produced. And a matrix polymer is added to this nonaqueous electrolyte, it agitates well, a matrix polymer is dissolved, and a sol-like electrolytic solution is obtained.

[0038] Next, specified quantity spreading of this electrolytic solution is carried out



on positive-active-material layer 2a. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on positive-active-material 2a.

[0039] Next, the positive-electrode sheet with which the gel electrolyte layer 4 was formed is cut down to band-like. And the lead wire made from aluminum is welded to the agenesis part of positive-active-material layer 2a of positive-electrode charge collector 2b, and it considers as the positive-electrode terminal 8. Thus, the band-like positive electrode 2 with which the gel electrolyte layer 4 was formed is obtained.

[0040] moreover -- as a negative electrode 3 -- the powder of a negative-electrode active material, and binders, such as polyvinylidene fluoride, -- homogeneity -- mixing -- further -- solvents, such as dimethyl formaldehyde and n-methyl pyrrolidone, -- adding -- a paste-like negative electrode -- a mixture is prepared, by [ which are set to negative-electrode charge collector 3b in it ] applying to homogeneity and drying, for example on metallic foils, such as copper foil and a nickel foil, negative-electrode active material layer 3a is formed, and a negative-electrode sheet is produced. the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture.

[0041] Next, the gel electrolyte layer 4 is formed on negative-electrode active material layer 3b of a negative-electrode sheet. In order to form the gel electrolyte layer 4, specified quantity spreading of the electrolytic solution first prepared like the above is carried out on a negative-electrode active material layer. Then, by cooling at a room temperature, a matrix polymer gels and the gel electrolyte layer 4 is formed on negative-electrode active material 3b.

[0042] Next, the negative-electrode sheet with which the gel electrolyte layer 4 was formed is cut down to band-like. And the lead wire made from nickel is welded to the agenesis part of negative-electrode active material layer 3a of negative-electrode charge collector 3b, and it considers as the negative-electrode terminal 9. Thus, the band-like negative electrode 3 with which the gel electrolyte layer 4 was formed is obtained.

[0043] And the side in which the gel electrolyte layer 4 was formed in the band-like positive electrode 2 and band-like negative electrode 3 produced as mentioned above is made to counter, and a separator 5 is allotted between a positive electrode 2 and a negative electrode 3, and it considers as an electrode layered product between. Furthermore, this electrode layered product is wound around a longitudinal direction, and it considers as the cell component 6.

[0044] The last pinches this cell component 6 with the sheathing film 7 which consists of an insulating material, and the resin film 10 is arranged on the part with which the positive-electrode terminal 8 and the negative-electrode terminal 9, and the sheathing film 7 lap. And the periphery edge of the sheathing film 7 is obturated, and while putting the positive-electrode terminal 8 and the negative-electrode terminal 9 between the obturation section of the sheathing film 7 and deriving outside, the cell component 6 is sealed in the sheathing film 7.

[0045] In case the cell component 6 is packed on the sheathing film 7, by arranging the resin film 10 on a contact part with the sheathing film 7, the positive-electrode terminal 8, and the negative-electrode terminal 9, the short-circuit in the weld flash of the sheathing film 7 etc. is prevented, and an adhesive property with the sheathing film 7, the positive-electrode terminal 8, and the negative-electrode terminal 9 improves.

[0046] Although especially an ingredient will not be limited if an adhesive property is shown to the positive-electrode terminal 8 and the negative-electrode terminal 9 as an ingredient of the above-mentioned resin film 10, as for polyethylene, polypropylene, denaturation polyethylene, denaturation polypropylene, these copolymers, etc., it is desirable to use what consists of

polyolefin resin. Moreover, as for the thickness of the above-mentioned resin film 10, it is desirable that it is the range of 20 micrometers - 200 micrometers by the thickness in front of thermal melting arrival. If it will be dealt with if the thickness of the resin film 10 becomes thinner than 20 micrometers, and a sex worsens and it becomes thicker than 300 micrometers, it will become difficult to become easy to penetrate moisture and to hold the airtightness inside a cell.

[0047] And in the condition of having packed with the sheathing film 7, while pressurizing the cell component 6 from the upper and lower sides, it heat-treats to the cell component 6. The cell component 6 packed with the sheathing film 7 can be pressurized, and the nonaqueous electrolyte held at the matrix polymer in a gel electrolyte can be effectively infiltrated into an electrode active material layer by heat-treating further. By infiltrating nonaqueous electrolyte into an electrode active material layer, the adhesion of the gel electrolyte layer 4 and an electrode active material layer was strengthened, it shall have high capacity and the gel electrolyte cell 1 obtained should be excelled in the charge-and-discharge property.

[0048] Since an electrolyte can be made to permeate the porous section of a separator enough especially when the positive electrode 2 with which the gel

electrolyte layer 4 was formed, and the negative electrode 3 of each other with which the gel electrolyte layer 4 was formed are piled up and it constitutes them through a separator 5, the effectiveness is large.

[0049] At this time, the temperature of heat-treatment has the desirable thing to the cell component 6 to do to more than the sol-gel transition temperature of a gel electrolyte. The direction at the time of being in a sol condition has a fluidity higher than the time of being gel, and this is because the nonaqueous electrolyte in a gel electrolyte layer can shorten penetration and heating pressurization time amount which becomes empty to an electrode active material layer.

[0050] The temperature of heat-treatment has the desirable thing to the cell component 6 to consider as the range of 50 degrees C - 105 degrees C, and, specifically, it is still more desirable to consider as the range which is 70 degrees C - 100 degrees C. If whenever [ stoving temperature ] is too higher than 105 degrees C, a part of non-aqueous solvent in a gel electrolyte will pyrolyze, and the cell capacity for which it asks will no longer be obtained. Moreover, when whenever [ stoving temperature ] is lower than 50 degrees C, the penetration of the nonaqueous electrolyte to the inside of an electrode active material layer becomes inadequate, and also the penetration of the nonaqueous electrolyte to

the inside of an electrode active material layer will take time amount, and productivity will fall.

[0051] Moreover, as for the pressure applied to the cell component 6, it is desirable to consider as the range of 490kPa-2450kPa. When a pressure is lower than 490kPa(s), the adhesion between the gel electrolyte layer 4 and an electrode active material layer becomes inadequate, and the charge-and-discharge property for which it asks is not acquired. Moreover, when a pressure is higher than 2450kPa(s), the gel electrolyte layer 4 will be crushed and will be destroyed.

[0052] Here, the pressurization and heating to the cell component 6 packed in the sheathing film 7 are performed by putting the sheathing film 7 from the upper and lower sides with a metal heat block. At this time, it is desirable to allot the block which consists of heat-resistant rubber between the sheathing film 7 and a heat block rather than to put the sheathing film 7 with a direct heat block, and to perform pressurization and heating to the cell component 6 in the sheathing film 7 through this block. If the sheathing film 7 is put with a direct heat block and \*\* thickness and heating are performed to the cell component 6, temperature maintenance of the heat block concerned will become difficult, and will become

unstable [ temperature ], and also the uniform pressurization control to the cell component 6 will become difficult. Therefore, by minding the block which consists of heat-resistant rubber, to the cell component 6, it is stabilized in homogeneity and pressurization and heating can be performed to it.

[0053] A cell object is acquired according to the above process.

[0054] Next, in order to activate the acquired cell object, a cell object is charged on predetermined charge conditions. And the charged cell object is discharged on predetermined discharge conditions. What is necessary is just to set up suitably the charge-and-discharge conditions in this case if needed [, such as a configuration of a cell, and magnitude, ].

[0055] Here, when the solvent in a gel electrolyte decomposes in the case of the above-mentioned activating charge, gas will occur. There was a problem that the cell capacity for which a lithium ion cannot fully move among two poles except that a clearance local between the electrode active material layer and gel electrolyte layers 4 in case this gas occurs is made, the adhesion between the electrode active material layer and gel electrolyte layers 4 is spoiled in this part, degradation of the cell voltage under preservation is large, there is much generating of a defective and the manufacture yield falls, but it asks as a result

was unrealizable.

[0056] So, in this invention, while pressurizing the cell object with which activating charge and discharge were made from the upper and lower sides, it heat-treats to a cell object. The cell object packed with the sheathing film 7 is pressurized, and by heat-treating further, even if a clearance is made between the gel electrolyte layer 4 and an electrode active material layer by the gas which occurred on the occasion of the above-mentioned activating charge process, a gel electrolyte and an electrode can be stuck. By maintaining the adhesion of the gel electrolyte layer 4 and an electrode active material layer, there shall be no poor electrical potential difference about the gel electrolyte cell 1 obtained, and it shall have high capacity, and should excel in the charge-and-discharge property.

[0057] As for the temperature of the heat-treatment to a cell object, at this time, it is desirable to carry out to more than the sol-gel transition temperature of a gel electrolyte. As for the temperature of the heat-treatment to a cell object, it is desirable to consider as the range of 50 degrees C - 105 degrees C, and, specifically, it is still more desirable to consider as the range which is 70 degrees C - 100 degrees C. If whenever [stoving temperature] is too higher than 105 degrees C, a part of non-aqueous solvent in a gel electrolyte will pyrolyze, and



the cell capacity for which it asks will no longer be obtained. Moreover, when whenever [ stoving temperature ] is lower than 50 degrees C, adhesion becomes inadequate about a gel electrolyte and an electrode, and also sticking a gel electrolyte and an electrode will take time amount, and productivity will fall.

[0058] Moreover, as for the pressure applied to a cell object, it is desirable to consider as the range of 490kPa-2450kPa. When a pressure is lower than 490kPa(s), the adhesion between the gel electrolyte layer 4 and an electrode active material layer becomes inadequate, and the charge-and-discharge property for which it asks is not acquired. Moreover, when a pressure is higher than 2450kPa(s), the gel electrolyte layer 4 will be crushed and will be destroyed.

[0059] Here, the pressurization and heating to a cell object are performed by putting the sheathing film 7 from the upper and lower sides with a metal heat block. At this time, it is desirable to allot the block which consists of heat-resistant rubber between the sheathing film 7 and a heat block rather than to to put the sheathing film 7 with a direct heat block, and to perform pressurization and heating to the cell object in the sheathing film 7 through this block. If the sheathing film 7 is put with a direct heat block and \*\* thickness and heating are performed to a cell object, temperature maintenance of the heat

block concerned will become difficult, and will become unstable [ temperature ], and also the uniform pressurization control to a cell object will become difficult. Therefore, by minding the block which consists of heat-resistant rubber, to a cell object, it is stabilized in homogeneity and pressurization and heating can be performed to it.

[0060] The gel electrolyte cell 1 is completed as mentioned above.

[0061] Even if a clearance is made by the gel electrolyte cell 1 produced with the application of this invention between a gel electrolyte layer and an electrode active material layer by the gas which occurred on the occasion of the above-mentioned activating charge process, it can restore the clearance, can maintain the adhesion between a gel electrolyte layer and an electrode active material layer, and can improve the manufacture yield. And the cell produced by making it such moves the lithium between forward negative electrodes smoothly, is closed, and becomes what has high capacity and was excellent in the charge-and-discharge property. Furthermore, the gel electrolyte cell 1 produced with the application of this invention becomes the thing excellent also in the dependability in an elevated temperature.

[0062] In addition, although the case where carried out the laminating of the

band-like positive electrode 2 and the band-like negative electrode 3, and wound around the longitudinal direction further and it considered as the cell component 6 was mentioned as the example and the gestalt of operation mentioned above explained it, this invention is not limited to this, and when the laminating of the rectangle-like positive electrode 2 and the rectangle-like negative electrode 3 was carried out and being considered as the electrode layered product, or also when an electrode layered product is folded up by turns, it can be applied.

[0063] The gel electrolyte cell 1 concerning a gestalt of this operation which was mentioned above is not limited especially about the configuration, and can be made into a thin shape and the various magnitude of large-sized \*\*. Moreover, this invention is [ primary cell ] applicable also about a rechargeable battery.

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#### EXAMPLE

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[Example] As shown below, the cell was produced and the effectiveness of this invention was checked.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the perspective view showing the example of 1 configuration of the gel electrolyte cell of this invention.

[Drawing 2] It is the perspective view showing the condition that a cell component is held into a sheathing film.

[Drawing 3] It is a sectional view in an A-B line among drawing 2 .

[Drawing 4] It is the perspective view showing the configuration of a positive electrode.

[Drawing 5] It is the perspective view showing the configuration of a negative electrode.

[Drawing 6] It is drawing having shown the relation between elapsed time and an electrical potential difference about the cell of an example and the example 1 of a comparison.

### [Description of Notations]

1 Gel Electrolyte Cell 2 Positive Electrode 3 Negative Electrode 4 Gel Electrolyte

Layer, 5 Separator 6 Cell Component 7 Sheathing Film 8 Positive-Electrode

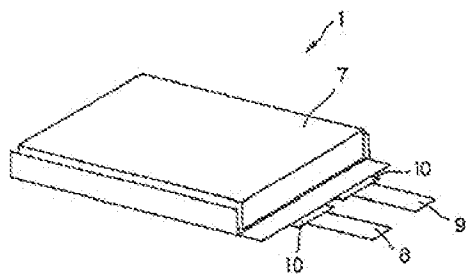
Terminal 9 Negative-Electrode Terminal 10 Resin Film

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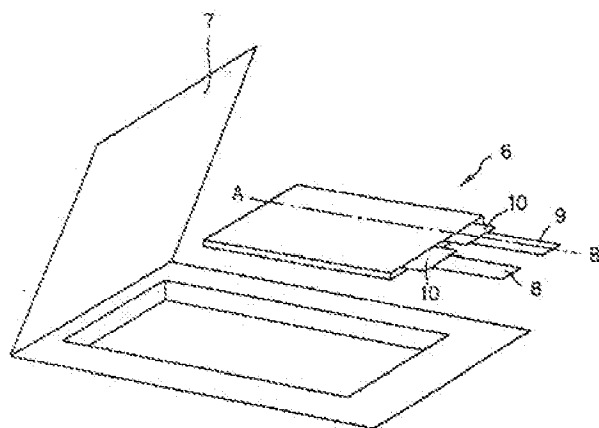
## DRAWINGS

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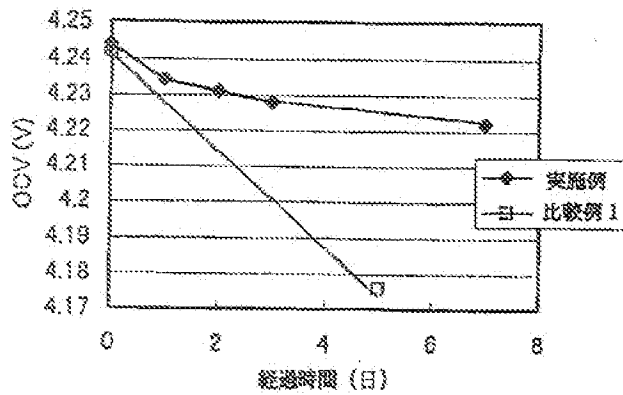
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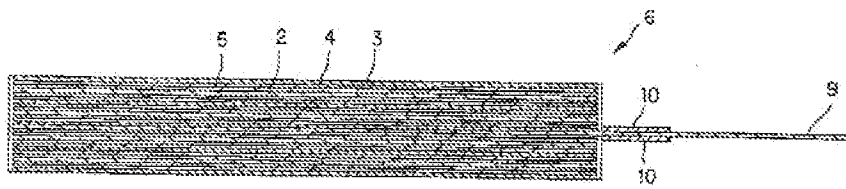
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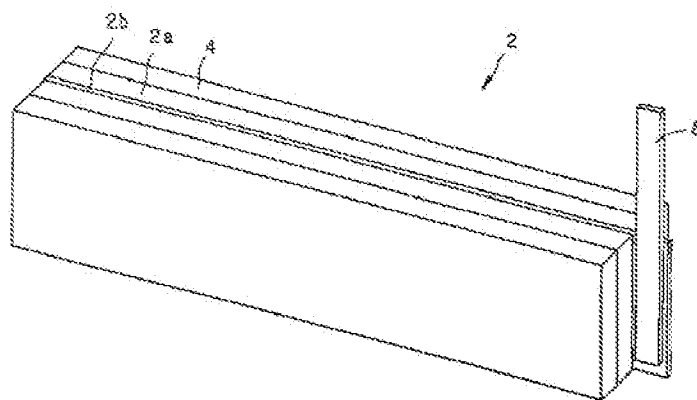
[Drawing 6]



[Drawing 3]



[Drawing 4]



[Drawing 5]

